Final Report for Project
"Properties of Transition Metal Atoms and Ions"

D. R. Beck, PI

DOE Grant #DE-FG02-92ER14292
Date Prepared: November 13, 2007

Research Accomplishments

At the time this project began (1992), there were no good *ab initio* treatments of the technologically important (plasmas, deep-level traps in semi-conductors, hydrogen storage devices, advanced lighting sources, atomic clocks, rare earth magnets, high temperature superconductors, etc) transition metal (TM) and rare earth (RE) atoms and ions.

Computationally, the difficulty arose from several sources: the need to treat relativity and correlation effects simultaneously, the complexity associated with open d or open f subshells, the near degeneracies present, the incomplete collapse of the d or f subshell radial functions, etc.

In the late 1970's the PI had begun to develop a Relativistic Configuration Interaction methodology, based on the formalism of Grant [Adv. Phys. 19, 747 (1970)] and the radial algorithms present in the Desclaux code [Comp. Phys. Commun. 9, 31 (1975)]. Throughout the 1980's new property packages were added [f-values and a "crude" treatment of resonances] and calculations were done for electron affinities of some of the "simpler" transition metals, as well as f-values. The only *ab initio* work competitive with what we were doing was the GRASP suite of codes [Dyall *et al*, Comp. Phys. Comm. 55, 425 (1989)], but it too was limited to "less complex" problems, and I felt I had a better understanding of which correlation effects were important (see below) based on past experience (since the 1960's)

In the early 1990's the PI spent a few summer weeks at Argonne National Lab, and became aware of the TM Hyperfine Structure measurements being made by Childs, Young and Berrah, which were tied to plasma fusion research of interest to DOE. They observed that single configuration Dirac-Fock calculations were able to describe a good portion of the measured hfs well, but other results were in poor agreement. After some thought, the PI suggested that this was due to missing correlation effects involving $3d^{n-1}4s$ basis functions. The PI added a hfs package to his RCI codes, and com-

pleted calculations on Sc II which removed the discrepancy there (published in 1992).

Based on this work, supported by the ANL "group" , and the PI's experience, a DOE proposal was prepared by the PI, submitted and funded. The initial work was on TM hfs for Ti I, II, Zr II and Nb II, where it was found that hfs for $3d^n$ and $3d^{n-2}4s^2$ levels would be systematically in error, if $3d^{n-1}4s$ basis functions were not present, and correctly positioned. This is because the open 4s subshell "carries" a very large hfs contribution. Next, some discrepancies were noted (by Childs) in the hfs structure of La II, which he thought were due to second order effects, which the PI was able to confirm. One of the last hfs calculations done was for Ta II $[(5d+6s)^4]$ because of Cowley's need for them in astrophysical abundances. At the time (2001) they represented the limit of what was possible for our RCI hfs methodology.

During this period (1995) we also got interested in computing TM f-values, for several reasons: (1) lifetimes of TM's were being measured at ANL, (2) we could "re-use" hfs TM wavefunctions (though new ones would also be needed), (3) they were of great practical interest, and not widely available (at an *ab initio* level), (4) we had the RCI methodology, and previous experience with f-values (starting with the PI's Ph.D. project). The first results were for Nb II (1995) and with the addition of Euri (a postdoc; Ph.D. Notre Dame with Walter Johnson) we were able to do some Relativistic Many Body Calculations on Kr I resonance transitions and remove the theoretical-experimental discrepancies by properly treating electron correlation effects. This work [10] also provided calculations and analysis for Ar, where we pointed out there were inconsistencies in some of the experimental error estimates.

At about the same time, lifetimes in Au^{66+} and Br^{22+} were obtained. A principle finding of this work was noting the importance of the QED corrections to energy differences–and the lack of a good methodology (still true) to "pin these down" to 1 eV or less. A Landé g-value package was added to the RCI codes; these can be very helpful (when experimentally available) in determining whether *ab initio* basis function mixing is accurate. Correct mixing can be essential to determination of accurate properties (a finding emphasized in our Fe f-value work, described below).

In the mid 1990's our attention was drawn to problems in determining the energy splitting within the $3d^4$ Ti I isoelectronic sequence. The $J = 2 \rightarrow J = 3$ energy difference was observed to be nearly independent of Z (very unusual) and it was proposed as a potential plasma diagnostic line. But it

was not possible (prior to our work) to reduce errors in energy differences to below 5%. We were able to reduce this error to ∼1% by more careful treatment of correlation and magnetic Breit effects for the observed levels [9] , and later predicted [12] W^{52+} and Bi^{61+} members [the Bi^{61+} was "spot on" a later measurement]

Our f-value calculations continued with a calculation for Tc I which was of interest to ANL [Atomic Trap Trace Analysis, being done by Linda Young]. Once again, this problem represented the then limit of *ab initio* calculations. Since Fe II was homologous to Tc I [meaning a lot of the Tc I angular data could be reused] and of great interest to astrophysicists [abundances], we did f-value calculations for that too. Since Fe ions have been the subject of much study, we made a considerable effort to improve our accuracy and efficiency at this stage. After our most recent Fe II and Fe III published results, the PI feels that the RCI methodology has matured to the point that it can reliably predict electric dipole f-values between any two levels lying below the first IP. In this regard, it becomes a full competitor with the best semi-empirical methods, which require a measured energy spectrum. For the present, such methods are the best way of predicting rare earth f-values. However, our most recent work on Gd IV aims to make RCI a full competitor here too. [Continuation of this work is funded by NSF now].

Work on f-values for Zr III, Nb IV, Mo V and Mo VI was also performed, stimulated by discussions with Joe Reader of NIST. This work included repositioning of the $5s^2$ level in Nb IV (since confirmed by Joe Reader's measurements]. A "new" phenomena was observed in Mo V, viz, the interleaving of $4p^5 4d^3$ "core-like" levels with the $4p^6 n\ell n'\ell'$ "valence" levels. For the computationalist, proper placement of these levels remains a challenge, as many more (large) correlation effects associated with the 4p "core" must be included-making proper relative placement of the levels difficult. This phenomena, present in many other atoms/ions [e.g. Yb I where 4f is involved, or in Tl II, where 5d is involved], will remain a challenge for years to come.

Calculated Magnetic Quadrupole (M2) lifetimes of $np^5(n+1)s$ J=2 rare gas states were not in good agreement with experiment. We fixed this by improving the correlation associated with the $np^5(n+1)d$ basis functions. We were also able to remove most of the discrepancies associated with K II $3p^6 \rightarrow 3p^5(4s+3d)$ J=1 f-values. The uppermost 3d state was particularly challenging, due to incomplete collapse of the 3d radial function for this state (in fact, a Dirac-Fock calculation for this radial failed).

Our final series of completed projects was to determine energies and f-

values for excitation or removal of 1s electrons in Kr II and III as well as Br I and Br II. These were of interest to ANL (Steve Southworth *et al*). These calculations were fairly extensive, including an Auger shift associated with the 1s hole. QED effects were large ($\sim$10 eV) and it is supposed that the inability to treat them beyond an exchangeless independent particle picture may well give rise to the bulk of the residual error of $\sim$1 eV. As noted above, treatment of QED for many electron atoms, including the effect of exchange and limited correlation effects is unlikely in the near term.

Executive Summary

Accomplishments of this project include: (1) improvement of the accuracy and efficiency of the RCI methodology to permit it to tackle almost all TM properties, and making good progress in extending these gains to the RE. Our improvements have stimulated improvements in the GRASP package, done by Froese Fischer. RCI efficiency gains are estimated to be $\sim$200$\times$ since the start of the project–about 10$\times$ from hardware improvements (originally DOE funded) and about 20$\times$ from software improvements. The net result is that currently the longest runs don't exceed 1 day. (2) identification and removal of systematic errors in several TM properties. To some extent, the PI became a "court of last resort" for experimenters who wondered why certain theoretical–experimental discrepancies existed. Auxiliary analysis codes were written and successfully used to improve the systematic understanding of correlation effects in TM and RE. This improved efficiency and a priori understanding of what new projects might involve. [Unsurprisingly, there are several cases which the PI was unable to resolve. Work on these is unpublished]. (3) education and training of graduate students and postdocs.

Ph.D. Students supported by DOE

5 Ph.D. students were supported by DOE; 4 have gotten their degrees, and the 5th will receive hers in Spring 2008. They are:

Debasis Datta	Ph.D. 1994
Konstantin Dinov	Ph.D. 1995
Steven M.O'Malley	Ph.D. 1999
Peggy Norquist	Ph.D. 2001
Lin Pan	Ph.D. Spring 2008

Postdocs supported

Euri Avgoustoglou	(1997-8)
Steven O'Malley	(2000-7)
Peggy Norquist	(2001)

Undergraduates

4 undergraduates did summer research on DOE projects (supported by MTU). One, David Oros, became a co-author of a publication. Another (Eric Domeier) is continuing on as an M.S. student (MTU supported)

Fellow, American Physical Society

In 2001, the PI was made a Fellow of the American Physical Society, partly in recognition of the DOE supported work he did.

26 Refereed Papers Published Acknowledging DOE Support

1. L. Young, C. A. Kurtz, D. R. Beck, and D. Datta, "Hyperfine studies in Zr II: Experiment and Relativistic Configuration Interaction Results" , Phys. Rev. A **48**, 173 (1993)

2. D. R. Beck and D. Datta, "Multi-Reference Relativistic Configuration Interaction Calculations for $(d+s)^n$ Transition Metal Atomic States: Application to Zr II Hyperfine Structure" , Phys. Rev. A. **48**, 182 (1993)

3. L. Young, S. Hasegawa, C. Kurtz, D. Datta and D. R. Beck, "Hyperfine Structure Studies of Nb II: Experimental and relativistic Configuration Interaction Results" , Phys. Rev, A **51**, 3534 (1995)

4. K. Dinov and D. R. Beck, "Electron Affinities and Hyperfine Structure for U^- and U I Obtained from Relativistic Configuration Interaction Calculations" , Phys. Rev. A **52**, 2632 (1995)

5. D. R. Beck and D. Datta, "Theoretical Lifetimes of Nb II z $4d^3 5p\ ^5G_3$ and $^3D_3$ Levels" , Phys. Rev. A **52**, 2436 (1995).

6. D. Datta and D. R. Beck, "Relativistic Many-Body Effects in the Fine and Hyperfine Structure of La II $(5d+6s)^2$ States: The Need for Second Order Electrostatic Corrections" , Phys. Rev. A **52**, 3622 (1995)

7. S. M. O'Malley and D. R. Beck, "Relativistic Configuration Interaction Results for Hyperfine Structure Constants of ^{133}Cs II and ^{137}Ba III $5p^5(5d+6s+6p)$ Levels" , Phys. Rev. A **54**, 3894 (1996).

8. D. R. Beck, "Hyperfine Structure Constants of $(d+s)^3$ states in La I and the Zr II and Hf II Isoelectronic Sequences" , Int. J. Quant. Chem. **65**, 555 (1997)

9. D. R. Beck, "Relativistic Configuration Interaction Results for Xe^{32+}, Ba^{34+}, Nd^{38+} and Gd^{42+} ^{5}D J=2 to J=3 Energy Differences" , Phys. Rev. A **56**, 2428 (1997)

10. E. N. Avgoustoglou and D. R. Beck, "Relativistic many-body Calculations for the oscillator strengths of the resonance lines of Neon, Argon, Krypton, and Xenon", Phys. Rev. A **57**, 4286 (1998)

11. D. R. Beck, "Theoretical Lifetimes and Landé g-values of Cs II $5p^5 6p$ Levels" , Phys. Rev. A **57**, 4240 (1998)

12. D. R. Beck, "Energy Differences and Magnetic Dipole Decay Rates for the W^{52+} and Bi^{61+} Members of the Nearly Z Independent $(3d_{3/2})^3 3d_{5/2}$ J=3 → J=2 Transition" , Phys. Rev. A **60**, 3304 (1999)

13. D. R. Beck and P. L. Norquist, "Lifetimes of $3s3p^2$ J=1/2, 5/2 Levels in Au^{66+} and Br^{22+}" , Phys. Rev. A **61**, 044504 (2000)

14. S. M. O'Malley, D. R. Beck, and D. P. Oros, "Oscillator Strengths, Landé g-values, and Hyperfine Structure for $3d^4 J$=0 → $3d^3 4p$ J=1 Transitions in Fe V" , Phys. Rev. A **63**, 032501 (2001)

15. P. L. Norquist and D. R. Beck, "*Ab Initio* Lifetimes, Landé g-values and Hyperfine Structure for Ta II states" , J. Phys. B **34**, 2107 (2001)

16. D. R. Beck, "Important Correlation Effects for the Er^{3+} $4f^{11}$ $^4S_{3/2}$ → $^4I_{15/2}$ Laser Transition Energy" , Int. J. Quant. Chem. **90**, 439 (2002)

17. S. M. O'Malley and D. R. Beck, "Lifetimes of Tc I $(4d+5s)^6 5p$ and $4d^6 5s\ ^6D$ States" , Phys. Scr. **68**, 244 (2003)

18. D. R. Beck, "Magnetic Quadrupole Lifetimes of $np^5(n+1)s$ J=2 States of Rare Gases" , Phys. Rev. A **66**, 034502 (2002)

19. D. R. Beck, "Oscillator Strengths for K II $3p^6$ to $3p^5(4s+3d)$ J=1 Transitions" , J. Phys. B **35**, 4155 (2002)

20. D. R. Beck and L. Pan, "*Ab Initio* Energy Levels, Oscillator Strengths, and Landé g values for J=0, 1 States of Zr III and Nb IV" , Phys. Scr. **69**, 91 (2004)

21. L. Pan and D. R. Beck, "Mo V J=0, 1 Energy Levels, Oscillator Strengths, and Landé g-values" , Phys. Scr. **70**, 257 (2004)

22. D. R. Beck, "*Ab Initio* Electric Dipole f values for Fe II $(3d^6 4s+3d^7)$ J=9/2→$3d^6 4p$ J=9/2 Transitions" , Phys. Scr. **71**, 447 (2005)

23. L. Pan, D. R. Beck and S. M. O'Malley, "Removal or Excitation of a 1s Electron in Kr II and Kr III" , J. Phys. B **38**, 3721 (2005)

24. L. Pan and D. R. Beck, "Mo VI J=3/2, 5/2 Energy Levels, Oscillator Strengths and Landé g-values" , Phys. Scr. **73**, 607 (2006)

25. L. Pan and D. R. Beck, "The 1s photoabsorption transitions in Br I and Br II" , J. Phys. B **39**, 4581 (2006)

26. D. R. Beck, "*Ab Initio* Electric Dipole f values for Fe II $(3d+4s)^7$ J=9/2→$(3d+4s)^6 4p$ J=11/2 Transitions" , J. Phys. B **40**, 651 (2007)

DAMOP Meetings/Abstracts

Additionally, the PI attended (frequently with a Ph.D student) and gave a Poster (acknowledging DOE support) at the annual DAMOP meeting throughout the funding period.